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Abstract

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PHYSICS

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FUNCTIONAL EXPANSIONS IN THE THEORY OF STATISTICAL EQUILIBRIUM

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N. N. Bogolyubov ([1]) developed a very general formal method of the generating functional for finding distribution functions that describe molecular ordering in systems composed of a very large number of particles. The functional introduced by him in ([2]) may be interpreted physically as the canonical distribution of a system of interacting particles in an external field. The BBG chain of equations (Bogolyubov–Born–Green) takes the form of an equation for the statistical distribution of particles of an ideal gas in an external field. But in the presence of interactions between molecules the field has an operator character, since it contains the operation of functional differentiation. I. P. Bazarov ([3]) constructed the solution of a closed equation with variational derivatives for the Bogolyubov generating functional ([2]) in the case of short-range forces in the form of a series in powers of the density.

A current problem in the modern theory of the liquid state is the development of more refined expansions that would converge substantially faster than the known expansions in density, activity, or the interaction constant. A considerable strengthening of convergence is achieved if the source of the external field is taken to be groups consisting of n molecules fixed in space. In order to obtain a complete description of the ordering in the "molecular atmosphere" of the selected group, it is sufficient to know the unary conditional distribution function $F_1(1/\{n\})$, since conditional distribution functions of higher orders are expressed through the unary one. For example,

$$F_2(12/\{n\}) = \frac{F_{n+2}(12, \{n\})}{F_n(\{n\})} = F_1(1/2, \{n\}) \cdot (F_1(2/\{n\})$$

and so on. Recently Percus ([4]) developed an effective method for constructing integral equations for distribution functions, based on the functional expansion of the unary distribution function, taking as the functional argument the interaction with a selected group of molecules. He succeeded in reproducing the integral equation established by direct summation of irreducible integrals of a definite topological structure (the hyperchain approximation) ([5],[6]), as well as the integral equation derived earlier by the method of collective coordinates ([7]), which in accuracy surpasses both the hyperchain approximation and the BBG equation for the binary distribution function in the superposition approximation ([8]).

In the present communication a new closed functional equation with variational derivatives is formulated for the unary correlative functional introduced in the manner of Bogolyubov ([2]). The solution of this equation, constructed by means of a functional expansion in the unary distribution function, contains the results of Percus ([4]) as a special case.

Let us define the correlative functionals

$$F_n^N(\{n\}/\varphi_j) = Q_N^{-1}(\varphi_j) \int \cdots \int \exp\{-\beta U_N\} \prod_{i=1}^{N} \varphi(i) \, \frac{d\{N-n\}}{V^{N-n}}, \qquad (1)$$

where $\beta = 1/kT$, $U_N = \sum_{i \neq j}^{N} u(ij)$ is the potential energy of interaction of N molecules with one another, and $Q_N(\varphi_j)$ is the generating functional

$$Q_N(\varphi_j) = \int \cdots \int \exp\{-\beta U_N\} \prod_{i=1}^{N} \varphi(i) \, \frac{d\{N\}}{V^N}. \qquad (2)$$

The function $\varphi(j)$ is arbitrary. But expressions (1) and (2) can be given a physical meaning by setting $\varphi(j) = \exp\{-\beta\psi(j)\}$, where $\psi(j)$ is an external field. Then (2) coincides with Bogolyubov' s functional [(2)], studied in detail by Bazarov [(3)]. If, however, $\varphi(j)$ is chosen in the form $\exp\{-\beta U_{n,1}(\{n\}, j)\}$, where $U_{n,1}(\{n\}, j)$ is the interaction energy of the group $\{n\}$ with molecule j, the functional $Q_N(\varphi_j)$ can be interpreted physically as the configurational integral of a system of interacting particles in the field of a distinguished group of molecules.

The proposed method is based on the exact functional relations

$$F_n^N(\{n\}/\varphi_j) = Q_N^{-1}(\varphi_j) \exp[-\beta U_n(\{n\})] \prod_{i=1}^{n} \varphi(i) \, Q_{N-n}(\varphi_j \exp[-\beta U_{n,1}(\{n\}, j)]), \qquad (3)$$

$$F_n^N(\{n\}/\varphi_j) = F_{n-1}^N(\{n-1\}/\varphi_j) \, F_1^N(n/\varphi_j \exp[-\beta U_{n-1,1}(\{n-1\}, j)]), \qquad (4)$$

whose validity is easily verified by direct substitution. For $\varphi(j) = 1$, (4) can be written in another form:

$$F_1^N(1/\{n\}) = F_1^N(1/\varphi_j = \exp[-\beta U_{n,1}(\{n\}, j)]), \tag{5}$$

in which the connection between conditional distribution functions and correlation functionals is especially clear. Below we shall need the special form assumed by equation (4) for $n = 2$:

$$F_2^N(12/\varphi_j) = F_1^N(1/\varphi_j)\, F_1^N(2/\varphi_j \exp\{-\beta U(1j)\}). \tag{6}$$

Functionally differentiating (2) with respect to $\varphi(1)$, we find

$$v\varphi(1)\frac{\delta \ln Q_N(\varphi_j)}{\delta\varphi(1)} = F_1^N(1/\varphi_j). \tag{7}$$

Taking (3) into account, equation (7) can be represented as a closed equation for the functional $Q_N(\varphi_j)$,

$$v\varphi(1) = \frac{\delta \ln Q_N(\varphi_j)}{\delta\varphi(1)} = \frac{Q_{N-1}(\varphi_j \exp\{-\beta u(1j)\})}{Q_N(\varphi_j)}.$$

Solutions of this equation will be considered elsewhere. Here we note that the dependence of the generating functional $Q_N(\varphi_j)$ on the number of particles complicates the calculations. On the other hand, since the correlation functionals converge in the limit $N, V \to \infty$ ($v = V/N = \text{const}$), a closed equation for the limiting one-particle functional $F_1(1/\varphi_j) = \lim_{N\to\infty} F_1^N(1/\varphi_j)$ becomes of substantial interest; with a proper choice of $\varphi(j)$, it contains complete information about the physical properties and structure of the liquid. For this purpose we functionally differentiate (1) and pass to the limit $N \to \infty$:

$$v\varphi(n+1)\frac{\delta F_n(\{n\}/\varphi_j)}{\delta\varphi(n+1)} = -F_1(n+1/\varphi_j)F_n(\{n\}/\varphi_j) + F_{n+1}(\{n+1\}/\varphi_j).$$

For $n = 1$, in view of (6), we obtain the required closed equation

$$v\varphi(2)\frac{\delta \ln F_1(1/\varphi_j)}{\delta\varphi(2)} = -F_1(2/\varphi_j) + F_1(2/\varphi_j \exp\{-\beta u(1j)\}). \tag{8}$$

Following Percus [(4)], we shall seek the solution of (8) in the form of an expansion in the functional $F_1(1/\varphi_j)$ about the value corresponding to the condition $\varphi(j) = 1$,

bearing in mind that in spatially homogeneous systems $F_1(1) = 1$. Especially interesting and general results are obtained if the expansion is carried out in such a way that the coefficients themselves turn out to be functionals. Let us write, for the logarithm of the unary functional,

$$\ln\left[\frac{F_1(1/\varphi;\varphi_j')}{\varphi(1)\varphi'(1)}\right]=\ln\left[\frac{F_1(1/\varphi_j')}{\varphi'(1)}\right]+\frac{1}{v}\int G(1k/\varphi_j')[F_1(k/\varphi_j)-1]\,dk+\cdots, \quad (9)$$

where φ and φ' are regarded as functionally independent.

Let us functionally differentiate (9) with respect to $\varphi(2)$ and put $\varphi(j)=1$. Applying equation (8), we find

$$F_2(2/\varphi_j'\exp\{-\beta u(1j)\})-F_1(2/\varphi_j')=G_1(12/\varphi_j')+\frac{1}{v}\int G_1(1k/\varphi_j')[F_2(2k)-1]\,dk. \quad (10)$$

Here, according to (6), $F_2(2k/\varphi_j=1)=F_1(2/\varphi_j=\exp\{-\beta u(1j)\})$ is the binary distribution function. On the other hand, restricting ourselves in (9) to linear terms, putting $\varphi(j)=\exp\{-\beta u(1j)\}$ and taking (6) into account, we write

$$\ln F_1(2/\varphi_j'\exp\{-\beta u(1j)\})=$$

$$=-\beta u(12)+\ln F_1(1/\varphi_j')+\frac{1}{v}\int G_1(1k/\varphi_j')[F_2(2k)-1]. \quad (11)$$

Equations (10) and (11) make it possible to find the functional $G_1(12/\varphi_j')$

$$G_1(12/\varphi_j')=-\beta u(12)+F_1(2/\varphi_j'\exp\{-\beta u(1j)\})-$$

$$-F_1(2/\varphi_j')-\ln[F_1(2/\varphi_j'\exp\{-\beta u(1j)\})/F_1(1/\varphi_j')]$$

or, using (6):

$$G_1(12/\varphi_j')=-\beta u(12)+[F_2(12/\varphi_j')/F_1(1/\varphi_j')]-F_1(2/\varphi_j')-$$

$$-\ln[F_2(12/\varphi_j')/F_1(1/\varphi_j')F_1(2/\varphi_j')]. \quad (12)$$

Substitution of expression (12) into (11) gives an integral equation for the functional $F_2(12/\varphi_j')$

$$\ln[F_2(12/\varphi_j')/F_1(1/\varphi_j')F_1(2/\varphi_j')]=-\beta u(12)+\frac{1}{v}\int\{-\beta u(1k)+$$

$$+[F_2(1k/\varphi'_j)/F_1(1/\varphi'_j)] - F_1(k/\varphi'_j)-$$

$$-\ln[F_2(1k/\varphi'_j)/F_1(1/\varphi'_j)F_1(k/\varphi'_j)]\}[F_2(2k)-1]\,dk. \tag{13}$$

Taking into account the functional relation (4), we see that, with an appropriate choice of φ', equation (13) leads to integral equations for distribution functions of any order.

For $\varphi'(j) = 1$, (13) becomes

$$\ln F_2(12) = -\beta u(12) + \frac{1}{v}\int\{F_2(1k) - 1 - \beta u(1k)$$

$$-\ln F_2(1k)\}\,[F_2(2k)-1]\,dk, \tag{14}$$

coinciding with the hyperchain approximation. It is well known (5) that the hyperchain approximation includes all those integrals whose diagrams are formed from chains of different lengths composed of series of all possible parallel-connected chains of bonds. All these diagrams are obtained by successive iterations of (6) from a single bond, to which the function $f(12) = \exp\{-\beta u(12)\} - 1$ corresponds.

If we put $\varphi'(j) = \exp\{-\beta u(3j)\}$ and take into account that, according to (4) and (6),

$$F_3(123) = F_2(13)\,F_1(2/\varphi_j = \exp\{-\beta u(1j) - \beta u(3j)\}) =$$

$$= F_2(13)\,[F_2(12/\varphi_j = \exp\{-\beta u(3j)\})/F_1(1/\varphi_j = \exp\{-\beta u(3j)\})] =$$

$$= F_2(12/\varphi_j = \exp\{-\beta u(3j)\}),$$

we arrive at an integral equation for the ternary correlation function $\varphi_3(123) = F_3(123)/F_2(12)F_2(13)F_2(23)$, which describes deviations

from the superposition approximation,

$$\ln\varphi_s(123) = \frac{1}{v}\int\{F_2(1k)F_2(3k)\varphi_3(13k) - F_2(3k) - F_2(1k)+$$
$$+1 - \ln\varphi_3(13k)\}\,[F_2(2k)-1]\,dk. \tag{15}$$

In deriving (15) it is assumed that the binary distribution function satisfies equation (14). The topological structure of the solution of equation (15), like that of equation (14), is iterative in character. The initial term of the iterative procedure is obtained if one sets $\varphi_3 = 1$ under the integral sign. In this case we arrive at the generalized superposition approximation, found earlier by direct topological methods ([6]), and also within the framework of variational theory ([9]),

$$\ln \varphi_3(123) = \frac{1}{v} \int [F_2(1k) - 1]\,[F_2(2k) - 1]\,[F_2(3k) - 1]\, dk.$$

The method described can be applied to finding the coefficient in a linear expansion analogous in construction to expansion (9),

$$[F_1(1/\varphi'_j\varphi'_j)/\varphi(1)\varphi'(1)] = [F_1(1/\varphi'_j)/\varphi'(1)] + \frac{1}{v} \int H(1k/\varphi'_j)\,[F_1(k/\varphi'_j) - 1]\, dk, \tag{16}$$

where $H(12/\varphi'_j)$ is the coefficient that must be determined so that the functional equation (8) be satisfied. The final result has the form

$$\frac{F_2(12/\varphi'_j)}{F_1(2/\varphi'_j)} \exp\beta u(12) = F_1(1/\varphi'_j) + \frac{1}{v} \int \left\{ \left[\frac{F_2(1k/\varphi'_j)}{F_1(k/\varphi'_j)} - F_1(1/\varphi'_j) \right] [F_1(k/\varphi'_j) - 1] - \right.$$
$$\left. - \frac{F_2(1k/\varphi'_j)}{F_1(k/\varphi'_j)} [\exp\beta u(1k) - 1]\,[F_2(2k) - 1] \right\} dk. \tag{17}$$

If $\varphi'(j) = 1$, (17) becomes the Percus–Yevick equation ([7]) for the binary distribution function

$$F_2(12) \exp\beta u(12) = 1 - \frac{1}{v} \int [\exp\beta u(1k) - 1]\, F_2(1k)\, [F_2(2k) - 1]\, dk.$$

For other choices of $\varphi'(j)$, equation (17) makes it possible to calculate distribution functions of higher orders. In particular, if we set $\varphi'_j = \exp\{-\beta u(3j)\}$, we obtain an equation for the ternary distribution function

$$\frac{F_3(123)}{F_2(23)} \exp\beta u(12) = F_2(13) + \frac{1}{v} \int \left\{ \left[\frac{F_3(13k)}{F_2(3k)} - F_2(13) \right] [F_2(3k) - 1] - \right.$$
$$\left. - \frac{F_3(13k)}{F_2(3k)} [\exp\beta u(1k) - 1] \right\} [F_2(2k) - 1]\, dk.$$

Equations (13) and (17) can be refined by retaining the following quadratic terms in the initial expansions (9) and (16). We note in conclusion that the rapid convergence of expansions in the pair correlation functional makes it possible to develop effective methods for closing the recurrent equations for distribution functions, an example of which is the BBGKY chain of equations.

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Note: Figure translations are in progress. See original paper for figures.